

BROMINATION OF ARALKYL COMPOUNDS USING POTASSIUM BROMATE AND POTASSIUM BROMIDE IN ACIDIC MEDIUM

G V R SHARMA, K SOMESWARA REDDY & ALICE R. ROBERT

Department of Chemistry, GIT, GITAM University, Rushikonda, Visakhapatnam, Andhra Pradesh, India

ABSTRACT

A simple method for benzylic bromination of aralkyl compounds is being reported in this communication. A mixture of potassium bromate and potassium bromide in acidic medium is used for bromination.

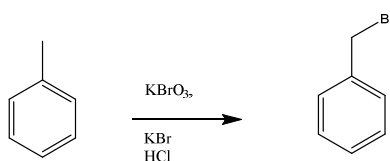
KEYWORDS: Aralkyl Compounds, Benzylic Bromination, Potassium Bromate, Potassium Bromide, Acidic Medium

INTRODUCTION

Halogenation of aromatic compounds is one of the most important reactions in organic synthesis. Benzylic bromination is particularly of considerable interest in the synthesis of organic compounds of medicinal interest. Benzylic bromination is usually carried out using reagents such as bromine and light, NBS, boron tribromide, etc. However, each method has its own advantages and limitations. For example use of molecular bromine is not so much preferred due to handling problems. Use of N-bromosuccinimide (NBS) needs organic solvents and forms insoluble byproduct and hence not so comfortable on large scale usage.¹⁻⁵ Borontribromide is expensive and hence has limited use. This prompts us for the development of a simple method of benzylic bromination that is environment friendly. We herein report a simple method for the benzylic bromination of aralkyl compounds in this communication.

RESULTS AND DISCUSSIONS

Methyl aromatic compound is treated with a mixture of potassium bromate and potassium bromide in dilute hydrochloric acid either at room temperature or at moderately higher temperatures of 80°C for approximately 4 hours followed by usual workup afforded brominated product with slight impurities which was purified by silicagel column chromatography using hexane and dichloromethane as eluents to afford the monobrominated products reasonably in good yields apart from minor unidentified products. The products were characterized by ¹HNMR and found to be monobrominated products. The reaction involves the use of readily available reagents carried out in aqueous medium which is of contemporary interest.




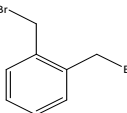

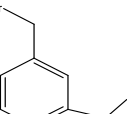
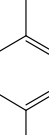
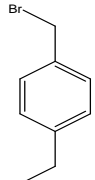
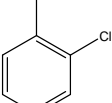
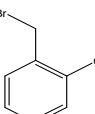
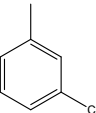
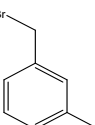
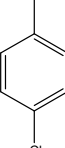
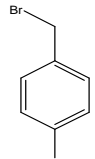



Experimental

In a typical experimental protocol, para xylene (1g, ~ 10 mmols), potassium bromate (2.4 g, ~ 20 mmols), potassium bromide (2.0 g, ~ 12 mmols) were taken in a 100 ml round bottom flask. To this water (10 ml) and conc. hydrochloric acid (15 ml) were added and heated at 80°C for 4 hours. Then dichloromethane (20 ml) is added,

washed with hypo, water, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silicagel chromatography using hexane and dichloromethane as eluents to afford the pure product in about 60% yield. ^1H NMR was recorded on 400 MHz using CDCl_3 as solvent. Methyl group disappeared at δ 2.0 and appeared a singlet at δ 4.5 for CH_2Br . Aromatic protons appeared at δ 7.2 and 7.5.

To test the methodology, reaction was carried out on several aralkyl compounds and tabulated the results in table 1. The products are characterized by ^1H NMR, IR and Mass. Also the reaction was carried out at different temperatures and found that the above conditions are appropriate. Some nitrogen containing methylaromatic compounds such as methyl pyridines were recovered as such without the formation of brominated products probably due to the formation of salts in the presence of hydrochloric acid.

Table 1

Reactant	Product	Yield(%)
		60
		55
		63
		60
		58
		62
	No reaction	
	No reaction	
	No reaction	

CONCLUSIONS

In conclusion, we herein report a simple brominating system using potassium bromate and potassium bromide in hydrochloric acid medium to provide the benzylic brominated compounds. Further optimization of the results is in progress which shall be communicated in due course.

ACKNOWLEDGEMENTS

One of the authors K. Someswara Reddy is grateful to the management of Bullaiah College for the support. Alice R. Robert is grateful to GITAM University for the encouragement through a minor research project.

REFERENCES

1. Hongbiao Chen et. al., *Synthetic Communications*, **40**, No 7, 998-1003, 2010
2. Yoel Sasson et. al., *Zeolites*, **13**, No.5, 341-347, 1993
3. Kiyoshi Tanemula et. al., *Chemistry Letters*, **32**, No.10, 2003
4. Yu Wu bin et. al., *Journal of Chemical Research*, **36**, No.5, 258-260. 2012
5. B. C. Ranu et. al., *Green Chemistry*, **10**, 232-237, 2008
6. Y. Nishina et. al., *Beilstein, J. Org. Chem.*, **9**, 1663-1667, 2013

